

Kondo effect of non-magnetic impurities and the co-existing charge order in the cuprate superconductors

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We present a theory of Kondo effect caused by an induced magnetic moment near non-magnetic impurities such as Zn and Li in the cuprate superconductors. Based on the co-existence of charge order and superconductivity, a natural description of the induced moment and the resulting Kondo effect is obtained in the framework of bond-operator theory of microscopic t - J - V Hamiltonian. The local density of state near impurities is computed in a self-consistent Bogoliubov-de Gennes theory which shows a low-energy peak in the middle of superconducting gap. Our theory also suggests that the charge order can be enhanced near impurities.

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Impurities in the cuprate superconductors have attracted much interest because of their role as an effective tool in probing the local electronic and magnetic properties of high T_c superconductors. Especially remarkable have been recent experiments in scanning tunneling microscopy (STM) [1,2] of surfaces of the cuprate superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) which showed a low-bias peak in the differential tunneling conductance in the vicinity of Zn impurities [1]. Since the Zn^{++} ion has spin $S = 0$, it seems natural to view each Zn site as just a potential scatterer, and therefore to interpret the peak as a quasibound state [3]. However, there are some experimental features which cannot be naturally explained by this theory [4].

More importantly, a series of NMR experiments [6,7] have shown clear evidences that there is an induced magnetic moment with spin $S = 1/2$ near Zn impurities. Therefore, it is imperative for a consistent theory to address the problem of impurity in the framework of Kondo effect. Though there have been several, previous works based on the Kondo physics [4,5], their approach was based on the *ad hoc* assumptions on the existence of induced spin moment near Zn impurities. Especially, the location of induced spin moment and the range of Kondo interaction were chosen in *ad hoc* manner. In this article, we would like to provide a self-consistent theory of Kondo effect based on the co-existence of charge order and superconductivity. We take this assumption to be natural because one of the important consequences of charge order is the induced $S = 1/2$ moment near non-magnetic impurities [8], as schematically shown in Fig.1.

Much more direct evidences for the relevance of charge order in the high T_c superconductors have been recently obtained in several remarkable STM experiments, one of which was performed by Hoffman *et al.* [9] where the charge order with a period of four lattice spacing was observed near vortex cores in BSCCO. As predicted in Ref. [8], the superconductivity is locally suppressed near the cores of vortices, and the static charge order ap-

pears in such regions. Another STM measurement in optimally doped BSCCO was performed by Howald *et al.* [10], showing clear evidences for the static charge order *even in zero magnetic field*. In addition to the STM measurements, inelastic neutron scattering techniques have been also used to provide important evidences for the charge order in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) [11,12].

Note our viewpoint that, though the charge order may not be static in all regions of superconducting phase, the time scale of charge order fluctuation is long enough to ensure the superconducting correlation and the Kondo spin physics. Therefore, in the rest of discussions, we will assume the static charge order with period of two lattice spacing (the spin-Peierls order), which, we believe, captures the essential physics in spite of its simplicity. Also, remember that the charge orders with different period are most likely to coexist because, as shown in Ref. [13], the periodicity is rather sensitive to various parameters including the doping concentration.

Recently, a natural theoretical framework was developed to describe the co-existing phase of charge density wave (CDW) order and superconductivity, based on the bond-operator representation [8]. It was shown that the saddle-point approximation of this bond-operator theory consistently interpolates the phase of Mott insulator at low dopings and that of superconductor with nodal fermions at moderate dopings. Therefore, it would be very interesting to explore the question whether the bond-operator theory gives rise to the low-energy peak of local density of state in the vicinity of non-magnetic impurities without *ad hoc* assumptions. It would be also interesting to study the effect of impurity on the charge order.

Now we begin our bond-operator theory by setting up the exact mapping between the bond operators and the usual electron creation operators [8]. Let c_{1a}^\dagger and c_{2a}^\dagger ($a = \uparrow, \downarrow$) be the electron creation operators on the two sites of a pair. When we project out all states with two

electrons at the same site, the electronic Hilbert space for a pair of sites is composed of nine states which can be expressed in terms of the “bond particle” creation operators defined by:

$$s^\dagger|v\rangle = \frac{1}{\sqrt{2}}\varepsilon_{ab}c_{1a}^\dagger c_{2b}^\dagger|0\rangle, \quad (1)$$

$$t_\alpha^\dagger|v\rangle = \frac{1}{\sqrt{2}}\sigma_{bc}^\alpha\varepsilon_{ca}c_{1a}^\dagger c_{2b}^\dagger|0\rangle, \quad (2)$$

$$h_{1a}^\dagger|v\rangle = c_{1a}^\dagger|0\rangle, \quad (3)$$

$$h_{2a}^\dagger|v\rangle = c_{2a}^\dagger|0\rangle, \quad (4)$$

$$d^\dagger|v\rangle = |0\rangle \quad (5)$$

where $|0\rangle$ is the electron vacuum and $|v\rangle$ is an imaginary vacuum void of any bond particles. Remember that σ_{ab}^α ($\alpha = x, y, z$) are the Pauli matrices, and ε_{ab} is the second-rank antisymmetric tensor with $\varepsilon_{\uparrow\downarrow} = +1$. The operators s, d, t_α all obey the canonical boson commutation relations, while the h_{1a}, h_{2a} obey the canonical fermion relations. Since the total Hilbert space of these five bosons and four fermions is much larger than that of the physical nine states, we must impose the following constraint on the bond particle Hilbert space.

$$s^\dagger s + t_\alpha^\dagger t_\alpha + h_{1a}^\dagger h_{1a} + h_{2a}^\dagger h_{2a} + d^\dagger d = 1. \quad (6)$$

In the subspace constrained by Eq. (6) we can write the exact expressions for electron operators in terms of bond operators:

$$c_{1a}^\dagger = h_{1a}^\dagger d + \frac{1}{\sqrt{2}}\varepsilon_{ab}s^\dagger h_{2b} - \frac{1}{\sqrt{2}}\varepsilon_{ac}\sigma_{cb}^\alpha t_\alpha^\dagger h_{2b}, \quad (7)$$

$$c_{2a}^\dagger = h_{2a}^\dagger d + \frac{1}{\sqrt{2}}\varepsilon_{ab}s^\dagger h_{1b} + \frac{1}{\sqrt{2}}\varepsilon_{ac}\sigma_{cb}^\alpha t_\alpha^\dagger h_{1b}, \quad (8)$$

$$S_{1\alpha} = \frac{1}{2}(s^\dagger t_\alpha + t_\alpha^\dagger s - \varepsilon_{\alpha\beta\gamma}t_\beta^\dagger t_\gamma) + \frac{1}{2}\sigma_{ab}^\alpha h_{1a}^\dagger h_{1b}, \quad (9)$$

$$S_{2\alpha} = -\frac{1}{2}(s^\dagger t_\alpha + t_\alpha^\dagger s + \varepsilon_{\alpha\beta\gamma}t_\beta^\dagger t_\gamma) + \frac{1}{2}\sigma_{ab}^\alpha h_{2a}^\dagger h_{2b}, \quad (10)$$

where $\varepsilon_{\alpha\beta\gamma}$ is the third-rank antisymmetric tensor with $\varepsilon_{xyz} = +1$, and, as usual, the electron spin operator is defined as $S_\alpha = 1/2 c_a^\dagger \sigma_{ab}^\alpha c_b$.

Equipped with the bond-operator representation of electron operators, we now apply the Bogoliubov-de Gennes (BdG) theory to solve the t - J - V model in finite systems containing a single impurity with (infinitely) strong repulsion, U , which is defined by:

$$H = -t \sum_{\langle i,j \rangle} (c_{ia}^\dagger c_{ja} + c_{ja}^\dagger c_{ia}) + J \sum_{\langle i,j \rangle} S_{i\alpha} S_{j\alpha} \\ + V \sum_{\langle i,j \rangle} c_{ia}^\dagger c_{ia} c_{jb}^\dagger c_{jb} - \mu \sum_i c_{ia}^\dagger c_{ia} + U c_{i_0a}^\dagger c_{i_0a} \quad (11)$$

where i_0 denotes the position of impurity, and μ is the chemical potential. Also, it is implicitly assumed that all states with two electrons on any site have been projected

out. Written in terms of bond operators, the Hamiltonian is physically meaningful only when the constraint condition in Eq.(6) is satisfied simultaneously. In this article, as usual in the mean field theory, only the average of this constraint will be satisfied via the Lagrange multiplier method. Note, however, that the average is taken over quantum fluctuations, not over space, so that the constraint will be satisfied individually at each site.

While general techniques of the bond-operator method can be found in Ref. [14] in detail, several conceptual and technical points are worth mentioning, especially related to the impurity problem. (1) The nearest-neighbor Coulomb repulsion, V , is not only physically reasonable, but also gives rise to an important consequence. Without V , the pairing of holes primarily occurs through the condensation of d -bosons, which results in a very short-range s -wave-like pairing. It is only when the d -boson condensation is suppressed by a large V that the superconducting state develops d -wave-like pairing, and nodal fermions emerge. Remember that we do not make any assumptions either on the emergence of superconducting state or the symmetry of pairing. They are obtained as a natural consequence of our saddle-point bond-operator theory of t - J - V model at moderate dopings.

(2) The chemical potential, μ , should be determined by fixing the average hole concentration, x , in the region far away from the impurity. In our finite system, we first obtain the value of μ without introducing the impurity, and then use it for the case of impurity by assuming that the system size is large enough so that a single impurity does not change the chemical potential.

(3) The impurity potential, U , is taken to be infinitely repulsive so that electrons are completely depleted from the Zn site. In the bond-operator formalism, one of the h -fermions, say h_{1a} ($a = \uparrow, \downarrow$), is pinned at the unpaired site near the Zn impurity. (See Fig.1.) Of course, it is possible without charge order in the doped antiferromagnets that the electron escapes from the unpaired site all together, leaving the vacancy instead of lone spin moment. It is assumed, however, that the empty state is energetically unfavorable because of the similar reason why d -boson condensation is suppressed for large V .

(4) Finally, unlike the previous work in Ref. [5], there are now two sets of BdG equations both for the bosons (t_α) and the fermions (h_{1a} and h_{2a}). Consequently, the number of self-consistency conditions for the normal and anomalous exchange energies is greatly increased, which limits the system size significantly. The number of self-consistency equations is $11 \times N^2/2$ with N^2 being the number of sites. Also, note that the diagonalization of boson BdG matrix is not as straightforward as that of fermion BdG matrix. It is performed by using the method in Ref. [15].

The saddle-point theory is not yet complete alone with the aforementioned self-consistent BdG equations, but it still needs to determine the condensation density of s -

boson, $\langle s \rangle^2$, by minimizing the ground state energy. Similar to the chemical potential, the Lagrange multiplier associated with the constraint is first computed as a function of $\langle s \rangle^2$ for the situation when there is no impurity, by satisfying the constraint in the mean field level. Then, $\langle s \rangle^2$ is fixed to be the value minimizing the ground state energy, at which point the Lagrange multiplier is also fixed. Fig.2 shows the ground state energy as a function of s -boson condensation density which also can serve as an order parameter for the spin-Peierls order. After the impurity is introduced, the position-dependent condensation density, $\langle s_i \rangle^2$, is determined in turn by satisfying the constraint at each site with the Lagrange multiplier determined previously. In this way, it is guaranteed (at least in the mean field level) that the ground state energy is minimized and also the constraint is satisfied at the same time.

Now let us turn to the physical observables. As mentioned in the introduction, the local density of state (LDOS) can be obtained directly in the STM experiments through the measurement of differential tunneling conductance, which show a low-energy peak in LDOS near non-magnetic impurities while the superconducting coherence peak is greatly suppressed [1]. Theoretically, the local density of state can be computed in terms of the spectral function given by:

$$\rho(\mathbf{r}, \omega) = \text{Im } G^{ret}(\mathbf{r}, \omega + i\delta), \quad (12)$$

where the retarded electronic Green function, $G^{ret}(\mathbf{r}, \omega + i\delta)$, is obtained by using the usual analytic continuation from the time-ordered electronic Green function $G(\mathbf{r}, \tau) = \langle T_\tau c_a(\mathbf{r}, \tau) c_a^\dagger(\mathbf{r}, 0) \rangle$ ($a = \uparrow, \downarrow$). In the bond-operator formalism, the spectral function of electron on the site 1 of dimer located at \mathbf{r}_i is related to that of h_2 -fermion via:

$$\rho_1(\mathbf{r}_i, \omega) \cong -\frac{1}{2} \langle s_i \rangle^2 \text{Im } G_{h_2}^{ret}(\mathbf{r}_i, -\omega - i\delta), \quad (13)$$

where $G_{h_2}(\mathbf{r}_i, \tau) = \langle T_\tau h_{2a}(\mathbf{r}_i, \tau) h_{2a}^\dagger(\mathbf{r}_i, 0) \rangle$. The electronic spectral function at site 2 is related to that of h_1 -fermion in similar way. In Eq.(13) the approximation is made when the contribution from magnons (t_α) is ignored because they are high-energy modes.

To compare the theoretical LDOS with the differential tunneling conductance measured in STM experiments, we need to take into account some key properties of realistic surface structure of BSCCO. Between the superconducting CuO_2 layer and the STM tip, there is always the BiO layer formed in such a way that each Bi atom is located directly above each Cu or Zn atom. So it is reasonable to assume that the Bi atom will block tunneling currents from reaching the Cu/Zn atom directly below the STM tip, and so the STM measures the LDOS contributed by the four nearest-neighboring sites instead of the single site directly below the tip. [5,16]. Under

this assumption, the LDOS measured in STM experiments, $\langle \rho(\mathbf{r}_i, \omega) \rangle$, may be identified with an average of LDOS from the nearest-neighboring sites: $\langle \rho(\mathbf{r}_i, \omega) \rangle \propto \rho(\mathbf{r}_i + \hat{x}, \omega) + \rho(\mathbf{r}_i - \hat{x}, \omega) + \rho(\mathbf{r}_i + \hat{y}, \omega) + \rho(\mathbf{r}_i - \hat{y}, \omega)$. Fig.3 shows $\langle \rho(\mathbf{r}_i, E) \rangle$ near and far away from the Zn impurity as a function of energy E/J , where the LDOS near impurity is defined as $\langle \rho(\mathbf{r}_i, \omega) \rangle$ with \mathbf{r}_i indicating the position of the Zn impurity. Compared to the LDOS far away from the impurity, the low-energy peak (denoted by the arrow in graph) develops near the Zn impurity, while the coherence peak is somewhat reduced indicating the suppression of superconductivity, which is in a reasonably good agreement with STM measurements.

Another physical observable in which we are interested is the order parameter of charge order, or the spin-Peierls order parameter, $\langle s_i \rangle^2$. One of the main questions that we would like to answer in this article is how much the charge order is affected by the impurity. It is completely conceivable that the spin-Peierls order is locally reduced near impurity at the same time when the superconductivity is also suppressed. In the extreme case the spin-Peierls order can be completely destroyed while the $S = 1$ excitons start to condense locally so that the magnetic order emerges near the impurity: in the bond-operator formalism, $\langle t_\alpha(\mathbf{r}_i) \rangle \neq 0$ with \mathbf{r}_i indicating the neighboring sites of impurity. If so, it may imply the emergence of the spin density wave (SDW) near impurities. However, the $\langle s_i \rangle^2$ plotted as a function of the distance from impurity in Fig.4 shows the opposite behavior that overall the spin-Peierls order is not affected much by the presence of impurity after one lattice spacing. In fact, the spin-Peierls order is somewhat enhanced at the nearest-neighboring Cu site of the Zn impurity, which may suggest an interesting prediction that the static charge can be observed near the Zn impurities by using the STM techniques. Finally, note that the bottom panel of Fig.4 shows the equal-time spin-spin correlation within dimer, $S_{1i}^\alpha S_{2i}^\alpha = -\frac{3}{4} s_i^2 + \frac{1}{4} t_i^\dagger t_i$, which suggests basically the similar physics by showing that the effect of the spin $S = 1$ excitons is small.

In conclusion, we have applied the bond-operator method to address the problem of non-magnetic impurity such as Zn/Li in the high- T_c cuprate superconductors. It is shown that, without *ad hoc* assumptions, the low-energy peak of local density of state in the vicinity of impurity can be computed in the framework of bond-operator formalism. Also, it is predicted that the charge-density-wave order can be enhanced near Zn impurities.

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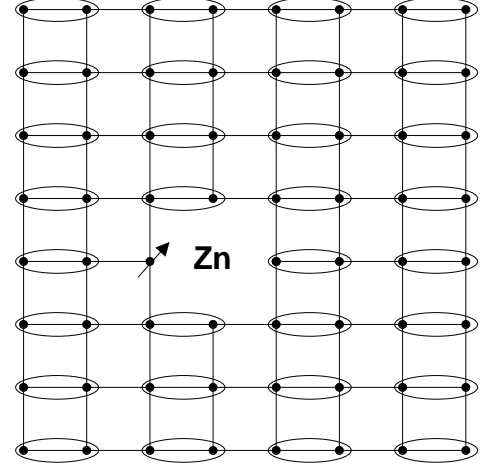


FIG. 1. Schematic diagram of the ground state of doped antiferromagnet with Zn impurity, which is assumed to have bond-centered charge order with period of two lattice spacing (columnal spin-Peierls order). Ellipses denote the valence bonds formed by two neighboring spins: $\frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)$. The arrow near Zn impurity indicates the induced spin moment. Note that a similar picture of moment formation applies to other charge order states.

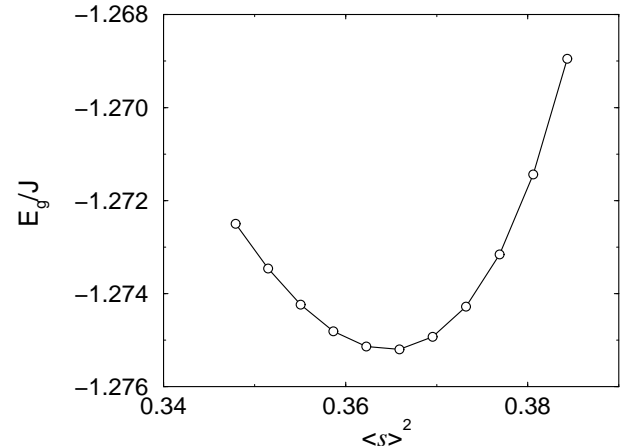


FIG. 2. Ground state energy as a function of the condensation density of s -boson for the square lattice system of 8×8 sites without the impurity. Here $t/J = 1.5$ and the hole concentration $x = 0.3$.

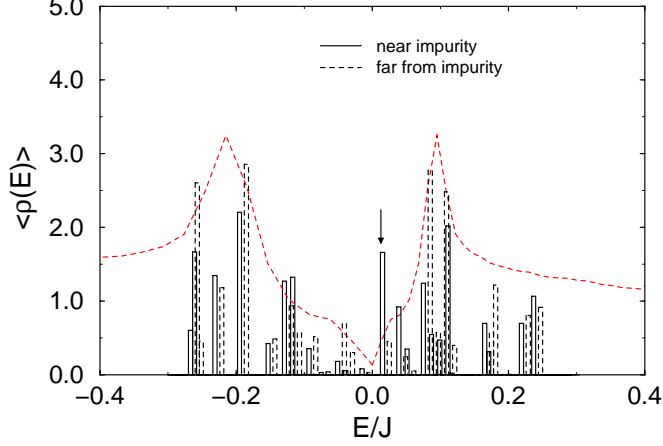


FIG. 3. Local density of state (LDOS) near the impurity (solid histograms) and far away from the impurity (dashed histograms) as a function of energy in the finite square-lattice system of 12×12 sites with $t/J = 1.5$ and $x = 0.3$. The dashed line is just a guide to eye for the LDOS far away from impurity, whose shape is obtained from the analytic computation for the uniform system, and is fitted roughly to follow the LDOS computed in finite system. Remember that the LDOS is not normalized due to the discrete nature of energy spectrum in finite system. It is important to note that the low-energy peak (denoted by arrow) develops in LDOS near the impurity, while the coherence peak is suppressed, which is in a good agreement with experiments.

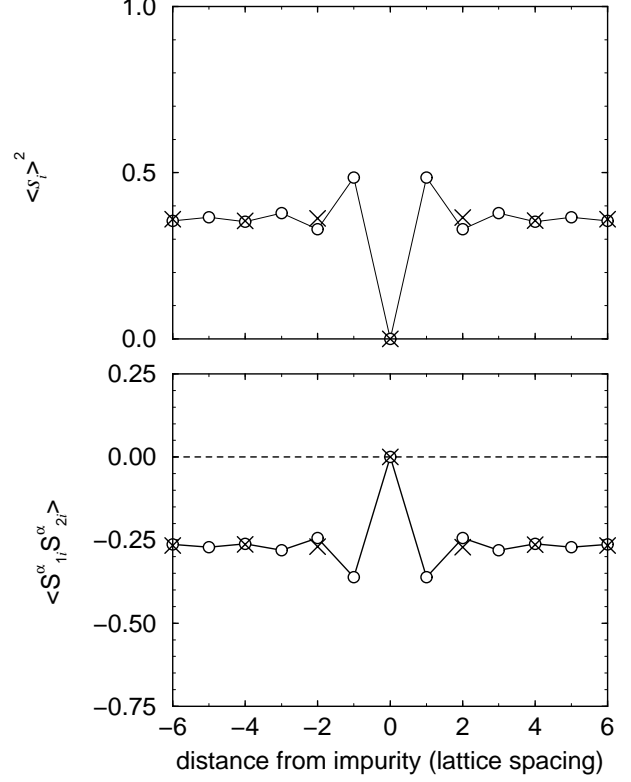


FIG. 4. Condensation density of s -boson, $\langle s_i \rangle^2$ (top panel), and the equal-time spin-spin correlation within dimer, $\langle S_{1i}^\alpha S_{2i}^\alpha \rangle$, (bottom panel) as a function of distance from the impurity in the finite square-lattice system of 12×12 sites with $t/J = 1.5$ and $x = 0.3$. Remember that in the bond-operator formalism $S_{1i}^\alpha S_{2i}^\alpha = -\frac{3}{4}s_i^2 + \frac{1}{4}t_i^\dagger t_i$ whose expectation value equals to $-3/4$ for the pure singlet valence bond, and $1/4$ for the pure triplet magnon. Of course, both the condensation density and the correlation are exactly zero at the impurity site since the Zn impurity is assumed to avoid electrons completely. Circles (crosses) in the graph are associated with the direction parallel (perpendicular) to the columnal spin-Peierls order. It is interesting to observe that the spin-Peierls order, or the charge density wave, is somewhat enhanced near the impurity while overall it is not affected much by the presence of impurity after one lattice spacing.